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NUCLEAR MAGNETIC RESONANCE STUDIES OF MOLTEN SALTS

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This report describes work in the areas of the measurement and interpretation of ^{13}C NMR chemical shifts of room temperature molten salts of various composition formed from aluminum chloride and 1-methyl-3-ethylimidazolium chloride; the measurement and interpretation of ^{27}Al NMR lineshapes as a function of temperature and melt composition; the NMR study of the reaction of acidic $AlCl_3$/1-methyl-3-ethylimidazolium molten salt with dissolved chlorine; and the redistribution of halide on aluminum during the mixing of acidic chloride and bromide melts in acetonitrile solvent. As part of the study of the effect of temperature on the ^{27}Al NMR lineshapes of the molten salts, a computer program is given which uses a matrix method to simulate NMR lineshapes as a function of chemical shifts and exchange rates.

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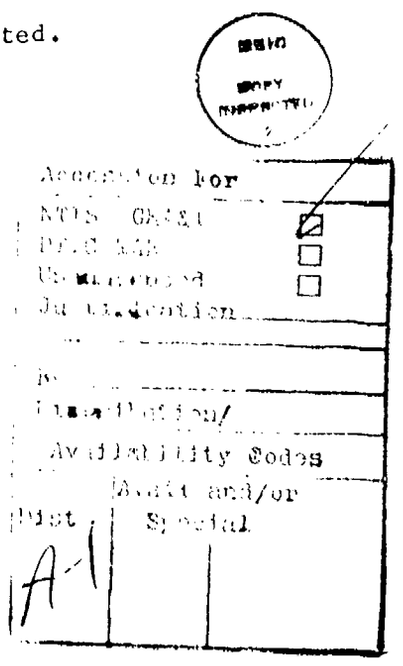

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SUMMARY

This report describes work in the areas of the measurement and interpretation of ^{13}C NMR chemical shifts of room temperature molten salts of various composition formed from 1-methyl-3-ethylimidazolium chloride and aluminum chloride; the measurement and interpretation of ^{27}Al NMR lineshapes as a function of temperature and melt composition; the measurement and interpretation of ^{27}Al NMR linewidths as a function of melt composition; the NMR study of the reaction of acidic $AlCl_3$/methylethylimidazolium molten salt with dissolved chlorine; and the redistribution of halide on aluminum during the mixing of acidic chloride and bromide melts in acetonitrile solvent.

As part of the study of the effect of temperature on the ^{27}Al NMR lineshapes of the molten salts, a computer program is given which uses a matrix method to simulate NMR lineshapes as a function of chemical shifts, linewidths, and exchange rates.

PREFACE

The work reported here is part of a continuing study of the structure and properties of molten salt electrolytes which have potential for use in high energy density electrochemical cells.

Part of this work has been accepted for publication in a forthcoming issue of Inorganic Chemistry.

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INTRODUCTION

The search for stable, room-temperature ionic liquids having high conductivity has led to the choice of molten salt mixtures of aluminum chloride/methylethylimidazolium chloride as a promising candidate for use as electrolytes in high energy-density batteries. Previous reports from this Laboratory have focused on the transport properties[1] and the proton NMR studies[2] of these room temperature molten salts. In addition, acidic aluminum chloride/dialkyl. 'iazolium chloride melts have recently been found to be excellent solvents for the electroplating of aluminum on various substrates.[3]

The research now being reported deals with the use of ^{13}C and ^{27}Al NMR spectroscopy to study the behavior of the chloroaluminate melts at various temperatures and to make comparisons with other molten salts systems, particularly aluminum chloride/N-butylpyridinium chloride molten salts that have been previously studied.[4-7] The two main advantages of the imidazolium chloride melts over the pyridinium chloride melts are first a larger liquid range at room temperature as the proportion of aluminum chloride is varied, and second, a wider electrochemical window in the imidazolium chloride melts compared to the N-butyl pyridinium melts.

In agreement with previous studies cited above, the two main equilibria involved in the melts studied in this work are

$$Im^+Cl^- + AlCl_3 = Im^+ + AlCl_4^- \quad (1)$$

in the concentration range from 0 to 0.5 mole fraction of $AlCl_3$, and

$$AlCl_4^- + AlCl_3 = Al_2Cl_7^- \quad (2)$$

in the concentration range from 0.5 to 0.66 mole fraction of $AlCl_3$. The equilibrium constants for both equilibria as written are both much greater than unity.

By studying the ^{13}C and ^{27}Al NMR spectra of the melts as a function of concentration and temperature, information can be obtained about their structure. The change in ^{13}C NMR chemical shifts of the carbon atoms of the imidazol ring, especially of the carbon atom between the two nitrogen atoms, should be a sensitive indicator of cation-anion interactions at various conditions, and thus give valuable information about the melt structures. The ^{27}Al spectra should give information about the type of chloroaluminate species present under various conditions, both by observation of the number of ^{27}Al resonances where separable, and also by observation of the ^{27}Al NMR linewidths at various conditions where only one resonance is observable.

EXPERIMENTAL

The chloroaluminate melts were prepared from purified $AlCl_3$ and 1-methyl-3ethylimidazolium chloride as described elsewhere.[8] In most cases the warm melts were stirred with a teflon-coated magnetic stirrer to facilitate uniform mixing. All preparations were done in a dry box under argon atmosphere, and the NMR samples were sealed in the dry box before removing to record their NMR spectra.

The nuclear magnetic resonance spectra were recorded using either a Nicolet NT-150 NMR spectrometer and a 12 mm tunable probe, or a JEOL FX-90Q NMR spectrometer using 10 mm or 5 mm tunable probes. During the NMR measurements, the temperature was controlled to about $\pm 1^{o}$ using NMR variable temperature control. The ^{13}C chemical shifts were referenced to an external TMS standard with positive shifts indicating decreased shielding.

RESULTS AND DISCUSSION

1. ^{13}C NMR Chemical Shifts of $AlCl_3$/Methylethylimidazolium Chloride Melts

A series of $AlCl_3$/1-methyl-3-ethylimidazolium chloride mixtures were prepared having mole fraction of $AlCl_3$ from 0 to 0.66 in order to study the effect of ^{13}C chemical shifts of the imidazolium carbon atoms as a function of concentration and temperature. At room temperature, the mixtures were liquid from about 0.3 to 0.6 mole fraction of $AlCl_3$, and at 90 ^{o}C the mixtures were liquid over the extended range of 0 to 0.66 mole fraction of $AlCl_3$. At these temperatures, well-defined ^{13}C NMR resonances were obtained in all cases. Figure 1 shows a comparison of the ^{13}C NMR spectra at room temperature of a melt of mole fraction $AlCl_3$ of 0.6 with the same melt dissolved in phosphoryl chloride. The two spectra are very similar, indicating that there is rapid averaging of the magnetic environment about the ^{13}C atoms in the neat melt analogous to that in phosphoryl chloride solution. The structure and carbon chemical shift assignments for the methylethylimidazolium cation are indicated in Figure 1.

The ^{13}C chemical shifts of the imidazolium (Im^{+}) ring should be governed by the number and type of counterion neighbors. In the basic region of melt composition of mole fraction $AlCl_3$ from 0 to 0.5, the two significant counterions are Cl^{-} and $AlCl_4^{-}$, while in the acidic region from 0 to 0.66, the two significant counterions are $AlCl_4^{-}$ and $Al_2Cl_7^{-}$. When the cationic species in a certain magnetic environment is rapidly exchanging with a species in another environment, only an averaged chemical shift will be observed for each carbon atom, with the observed shift given by the equation:

$$\delta_{obs} = \sum_y X_y \delta_y \qquad (3)$$

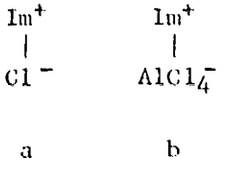
where X_y is the mole fraction of species y and δ_y is the chemical shift of species y. The chemical shift data allows models of the cation-anion species to be tested when reasonable values of the X_y and δ_y values can be obtained.

The ^{13}C chemical shift data obtained in this study for the six carbon atoms of the methylethylimidazolium cation as a function of melt composition showed that by far the greatest change in shift was observed for the C-2 carbon situated between the two imidazolium nitrogen atoms This is expected, since molecular orbital calculations show carbon C-2 of the imidazolium cation to have by far the smallest electron density; and thus, this carbon atom should be affected to the greatest degree by cation-anion interactions.

Table 1 shows the value of the C-2 chemical shift (referred to the external lock signal) at 90 ^{o}C as the mole fraction of $AlCl_3$ is increased from 0 to 0.6 . A plot of the measured ^{13}C chemical shifts for this carbon as a function of the mole fraction of $AlCl_3$ is shown in Figure 2. The greatest change is seen to be in the basic region of mole fraction $AlCl_3$ from 0 to 0.5. In this region, the reaction of Cl^- and $AlCl_3$ to yield $AlCl_4^-$ leads to the Cl^- counterion being replaced by $AlCl_4^-$ counterion, while in the acidic region of mole fraction $AlCl_3$ from 0.5 to 0.66, the reaction of $AlCl_4^-$ and $AlCl_3$ to yield $Al_2Cl_7^-$ leads to the counterion $AlCl_4^-$ being replaced by $Al_2Cl_7^-$ counterion. The former case thus leads to a much gr ater change in the magnetic environment of the C-2 carbon of the imidazolium cation than in the latter case, in which a chloroaluminate anion is being replaced by another chloroaluminate anion. Because of the marked change in chemical shift with composition in the basic region, the chemical shift data in this region can best be used to test models of the number and type of interactions occurring in the melt.

Two of the simplest models of the basic melt involve (1) ion pairs, or one ion-ion interaction per Im^+, and (2) two ion-ion interactions per Im^+. According to Model 1, the two species to consider in the basic region are:

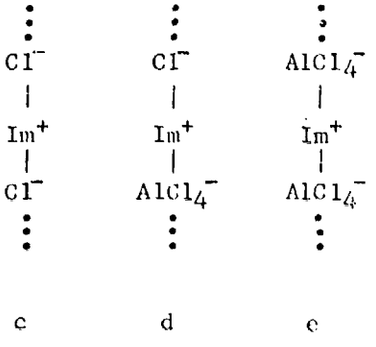
Model 1



a b

According to Model 2, the three species to consider in the basic region are

Model 2



c d e

Species c through e are not discrete, but represent portions of oligomeric chains of alternating cations and anions. When the different species are in fast chemical exchange, the observed chemical shifts should be the population weighted average of the various species present.

The theoretical C^{13} chemical shifts for Models a and b can be expressed

by the following equations,

$$\text{Model 1:} \quad \delta_{obs} = X_a\delta_a + X_b\delta_b \tag{4}$$

$$= (1-Y)\delta_a + Y_b\delta_b \tag{5}$$

$$\text{Model 2:} \quad \delta_{obs} = X_c\delta_c + X_d\delta_d + X_e\delta_e \tag{6}$$

$$= (1-Y)^2\delta_c + 2(Y-Y^2)\delta_d + Y^2\delta_e \tag{7}$$

where Y = mole fraction of $AlCl_4^-$.

Thus, Model 1 predicts a linear fit of a plot of chemical shift versus mole fraction of $AlCl_4^-$, while Model 2 predicts a quadratic fit. The X_i mole fractions can be obtained from the stoichiometries indicated in equations 1 and 2, assuming a random distribution of anions. Since the plot of the ^{13}C chemical shift of carbon C-2 at 90 ^oC versus mole fraction $AlCl_4^-$ is non-linear, as shown in Figure 3, the model of simple ion pairs is not in agreement with the experimental data. At least two or more ion-ion interactions must be present to explain the ^{13}C shift behavior. The fit shown for Model 2 was obtained by a least squares routine, and obeys the equation:

$$\delta_{obs} = (1-Y)^2(149.33) + 2(Y-Y^2)(149.05) + 2Y(146.85) \tag{8}$$

2. ^{27}Al Lineshapes of $AlCl_3$/Methylethylimidazolium Chloride Melts

A ^{27}Al NMR study of the $AlCl_3$/1-methyl-3-ethylimidazolium chloride melts was undertaken to determine if different chloroaluminate species could be detected as a function of concentration and temperature. In the basic region only one chloroaluminate species is expected, namely, $AlCl_4^-$. However, in the acidic region, at least two chloroaluminate species are predicted, $AlCl_4^-$ and $Al_2Cl_7^-$. Since the expected equilibrium reaction between these two species

$$Cl_3Al\text{-}Cl\text{-}AlCl_3^- + Al^*Cl_4^- = Cl_3Al^*\text{-}Cl\text{-}AlCl_3^- + AlCl_4^- \tag{9}$$

involves the breaking of an Al-Cl bond, the exchange of aluminum between

$AlCl_4^-$ and $Al_2Cl_7^-$ sites should be slow enough at room temperature so that the different chloroaluminate ions may be observed in the NMR spectra of the acidic melts. (In order to see separate resonances, the rate of exchange must be less than $1.414\ \pi\ \Delta\nu$, where $\Delta\nu$ is the chemical shift difference between the two resonances. Since this chemical shift difference is in the order of 10 ppm, the rate of exchange of Al that results in the resonances beginning to merge is approximately 10^3 sec^{-1}.)

The NMR results at room temperature verified that at both observation frequencies of 23.29 and 39.10 MHz, only one ^{27}Al resonance could be observed from mole fraction of $AlCl_3$ from 0 to 0.5; presumably the ^{27}Al resonance of $AlCl_4^-$. However, in the middle of the acidic region near mole fraction $AlCl_3$ of 0.6, it was possible to observe two different ^{27}Al NMR resonances.

Because of the quadrupole moment of the ^{27}Al nucleus and the fact that $Al_2Cl_7^-$ has a larger electric field gradient at the nucleus than $AlCl_4^-$ due to its lower symmetry, there is a greater broadening of the resonance linewidth for $Al_2Cl_7^-$ from efficient nuclear quadrupole relaxation (vide infra). The NMR results showed that longer delay times following the NMR pulses made it easier to detect two NMR resonances in the acidic region of about 0.6 mole fraction of $AlCl_3$. This is because the free induction decay (FID) of the broad line component of the NMR signal loses its intensity more rapidly than the narrow line component, so the subsequent Fourier transform of the collected FID signals shows an attenuated absorption signal for the broad line component. This is apparent in the ^{27}Al spectra of melt with mole fraction $AlCl_3$ of 0.56 as shown in Figure 4. In all cases, the NMR frequency was 39.104 MHz, the sweep width was 10 KHz, and the temperature was 30 ^{o}C. However, the preacquisition delay times from bottom to top of Figure 4 were .033, .50, and 1.0 ms, respectively, showing the

greater separation of the NMR resonances when a longer delay time was used. In agreement with a previous assignment of chloroaluminate anion NMR resonances in a study using $AlCl_3$/n-butylpyridinium acidic melts,[4] the narrow line component to high field is labeled the $AlCl_4^-$ resonance, while the broader downfield component is labeled the $Al_2Cl_7^-$ resonance.

The effect of temperature on the NMR lineshapes was investigated for a $AlCl_3$/methylethylimidazolium chloride melt having mole fraction $AlCl_3$ of 0.6. At this mole fraction of $AlCl_3$, the reaction

$$2Im^+Cl^- + 3AlCl_3 = AlCl_4^- + Al_2Cl_7^- + 2Im^+ \qquad (10)$$

yields approximately equal mole fractions of the $AlCl_4^-$ and $Al_2Cl_7^-$ ions. Figure 5 shows the effect of raising the temperature from 47 to 67 then 88 °C (bottom to top of Figure) using an observation frequency of 23.29 MHz and a preacquisition delay time of 1.5 ms. As the temperature is raised, the narrow and broad components of the resonance coalesce, with the averaged chemical shift falling in between the chemical shift of the broad and narrow components. Because of the decrease in viscosity of the melts with increasing temperature, the resonance lines are expected to narrow, but not to merge into one another. The coalescence of the resonances above 88 °C is indicative of rapid exchange of the Al nuclei between the tetra- and hepta- chloroaluminate anion species.

Assuming a 2-site exchange mechanism between $AlCl_4^-$ and $Al_2Cl_7^-$ as given in equation 9, the temperature-dependent line shapes can be calculated from the appropriate exchange matrix:

$$\text{Int} \propto \text{Re} \left| P_A, P_B \right| \begin{vmatrix} i(\omega-\omega_A) - 1/T_A - k_A & k_A \\ k_B & i(\omega-\omega_B) - 1/T_B - k_B \end{vmatrix}^{-1} \begin{vmatrix} 1 \\ 1 \end{vmatrix} \qquad (11)$$

The intensity of the resonance is proportional to the real part of the inverse of the exchange matrix, where i is the square root of -1, $(\omega-\omega_n)$ is the chemical shift in radians of nucleus n, and $T_n = 1/(\pi\Delta\nu_{1/2})$ is the

relaxation time of nucleus n in terms of its line width at half-height.

The constants k_A and k_B are the reciprocals of the average lifetimes τ_A and τ_B of nucleus A and B, respectively. Since the equations governing the determination of these quantities are not usually found in NMR texts and reviews, they will be briefly discussed. Following the method of Gutowsky and Saika,[9] let us consider the exchange of the labeled nuclei, M^*, between two sites, MA and MB:

$$M^*A + MB = MA + M^*B \tag{12}$$

In this example, the rate of change of M^*A with time is

$$-d(M^*A)/dt = k_2(M^*A)(MB) \qquad \text{(2nd order rate law)} \tag{13}$$

and since (MB) is constant in time, the labeled M^*A have an average lifetime, τ_A, given by

$$\tau_A = (M^*A)/\text{rate of exchange of } M^*A = 1/(k_2(MB)) \tag{14}$$

The exchange of MB is similar, with the average lifetime of M^*B given by

$$\tau_B = 1/(k_2(MA)) \tag{15}$$

For purposes of calculation, it is more convenient to express the concentrations (MA) and (MB) of equations 14 and 15 in terms of the mole fractions P_A and P_B:

$$\tau_A = \tau/P_B, \quad \text{and} \quad \tau_B = \tau/P_A \tag{16}$$

where $P_A = (MA)/[(MA)+(MB)]$, $P_B = (MB)/[(MA)+(MB)]$, and $\tau = 1/k_2[(MA)+(MB)]$. (17)

From the above equations, it is evident that k_A and k_B are determined by the equations:

$$k_A = P_B/\tau, \quad \text{and} \quad k_B = P_A/\tau, \tag{18}$$

where $$\tau = \tau_A\tau_B/(\tau_A+\tau_B). \tag{19}$$

Thus, these equations show that for the two-site exchange, the mole ratio and a single lifetime, τ, are sufficient to determine the shape of the simulated exchange-averaged NMR resonance. The NMR lineshapes calculated by the matrix

program given in Appendix I are identical in the two-site case to the equations of Rogers and Woodbrey[10] when $k_{1,2}$ is set equal to $1/\tau$.

The calculations were made as a USER subroutine attached to the PHD Database System.[11] Lines 1000 to 1930 shown in Appendix I detail the calculation of the NMR lineshape simulations. Using a chemical shift difference of 350 Hz for the two species, a mole fraction of 0.1 and 0.9 for the narrow and broad components, respectively; the three simulated spectra were obtained as shown in Figure 6. These simulated spectra show the correct lineshapes with the following values of τ, the preexchange lifetime, and the linewidths of the narrow and broad components, at 47, 67, and 88 °C: 0.0040 sec, 95 Hz, 1200 Hz; 0.0013 sec, 12 Hz, 710 Hz; and 0.0007 sec, 10 Hz, 600 Hz. It should be noted that the mole fraction values used of 0.1 and 0.9 have to be artificially adjusted due to the discrimination of the broad line component when a delay time of 1.5 ms is used, so they are not a true measure of the actual mole fractions of the anions.

The chemical shift difference of 350 Hz used in these simulations was needed to give the right shape to the 47° ^{27}Al spectrum. If only the high temperature results had been considered, the data could have been simulated more exactly using a smaller chemical shift difference. This leads us to propose that a three-site or higher exchange mechanism occurs in the acidic melts at these temperatures. For this reason, we believe the 2-site exchange simulations cannot be used to give an accurate value for the activation energy for this exchange.

A possible three-site exchange equilibrium for ^{27}Al in the acidic melts could involve an additional equilibrium between $Al_2Cl_7^-$ and a small amount of Al_2Cl_6 (of insufficient intensity to detect as a third ^{27}Al resonance at low temperature):

$$Al_2Cl_6 + Al^*Cl_4^- = Al^*AlCl_6 + AlCl_4^- \qquad (20)$$

3. ^{27}Al NMR Linewidths of $AlCl_3$/Methyethylimidazolium Chloride Melts

The linewidth at half-height ($\Delta\nu_{1/2}$) of an NMR resonance line having a Lorentzian lineshape is given by the well-known equation

$$\Delta\nu_{1/2} = 1/(\pi T_2) \tag{21}$$

where T_2 is the spin-spin relaxation time. Because ^{27}Al is a quadrupolar nucleus having a nuclear spin, I, of 5/2, the spin-spin relaxation process is dominated by the nuclear quadrupole relaxation mechanism, and is given by:[12]

$$1/T_2 = (3/40)((2I+3)/(I^2)(2I+1))(2\pi eQ/h)^2(d^2v/dz^2)\tau_c \tag{22}$$

where eQ is the nuclear quadrupole moment, d^2v/dz^2 is the maximum electric field gradient at the nucleus, and τ_c is the correlation time for molecular Brownian motion.

In the case of aluminum containing molecules, the electric field gradient can vary from very insignificant to very significant depending on whether the molecule has symmetrical bonds around the aluminum atoms and a symmetrical distribution of the electron density associated with each bond, or whether the molecule lacks this symmetry. In the former case, $1/T_2$ tends to be small and the NMR linewidth narrow, and in the latter case, the reverse is true, as indicated by equation 22 above. In addition, since the correlation time, τ_c, is approximately related to the viscosity, η, and the radius of the molecule, a, by

$$\tau_c \propto \eta a^3 \tag{23}$$

a high viscosity can also contribute to line broadening.

The ^{27}Al NMR resonances were observed at 90 ^{o}C for the $AlCl_3$/1-methyl-3-ethylimidazolium chloride melts over the composition range of mole fraction $AlCl_3$ from 0 to 0.66. The observation frequency was 39.10 MHz and the preacquisition delay time was 0.033 ms. The measured ^{27}Al linewidths are given in Table 2. The striking feature about the data is the marked decrease in $\Delta\nu_{1/2}$ to 2.34 Hz exactly at mole fraction $AlCl_3$ of

0.5. At this concentration, the melt is presumed to have the simple 1:1 cation-anion composition $Im^+AlCl_4^-$. Since the $AlCl_4^-$ ion has tetrahedral symmetry, the electric field gradient at the nucleus is at a minimum, and a narrow ^{27}Al is obtained in agreement with equation 22.

Table 2 also shows a large increase in the ^{27}Al linewidth at 90 ^{o}C as the mole fraction of $AlCl_3$ is decreased from 0.5 to 0. The bulk of this increase is probably due to the increasing viscosity of the melts which are richer in the organic halide. The increase in viscosity results in a proportional increase in molecular correlation time, which directly contributes to an increase in linewidth (equations 22 and 23).

The ^{27}Al linewidths were also measured at 30 ^{o}C in the acidic $AlCl_3$/methylethylimidazolium chloride melts at a frequency of 23.29 MHz. At this temperature and frequency, and a preacquisition delay time of .200 ms, only a single broad ^{27}Al resonance was observed. Table 3 gives the values of the measured linewidths at half-height as well as the corresponding viscosity of the melt at each concentration, computed at 30 ^{o}C from equations available from a previous study.[1]

As shown in Figure 7, the $\Delta\nu_{1/2}$ linewidths for ^{27}Al resonances of the acidic melts correlate roughly with the mole fraction of $Al_2Cl_7^-$ (calculated from the moles of $AlCl_3$ to moles of ImCl). As the melts are made more acidic, the concentration of unsymmetrical $Al_2Cl_7^-$ increases and the $\Delta\nu_{1/2}$ value also increases. However, equations 21, 22 and 23 show that the linewidth is also a function of the viscosity, increasing directly as the viscosity increases. Therefore, to normalize to unit viscosity, the linewidths were divided by the absolute viscosities and the resulting values plotted against the calculated mole fraction of $Al_2Cl_7^-$ as show in Figure 8. The interesting result is that there is a fairly linear relation shown by the plot until the mole fraction of $Al_2Cl_7^-$ reaches about 0.7,

followed by a marked increase in slope. This suggests that at large values of the heptachlorosluminate anion concentration, one or more additional unsymmetrical species are contributing to the ^{27}Al linewidths, perhaps such as Al_2Cl_6.

4. Reaction of $AlCl_3$/Methylethylimidazolium Chloride with Dissolved Chlorine

When Cl_2 gas is bubbled into an acidic $AlCl_3$/1-methyl-3-ethylimidazolium chloride melt, a reaction takes place as evidenced by changes in both the ^{13}C and ^{1}H NMR spectra. The evidence is consistent with the stepwise replacement of the protons at ring positions 4 and 5 with chlorine atoms. The proposed reaction is:

1-methyl-3-ethylimidazolium chloride + 4- and 5- chloro-1-methyl-3-ethyl-imidazolium chloride + 4,5-dichloro-1-methyl-3-ethylimidazolium chloride.

Figure 9 shows the change in the ^{1}H spectrum with time as a melt of composition 0.60 mole fraction $AlCl_3$ is reacted with dissolved chlorine at room temperature. As predicted by the above reaction sequence, the three proton resonances downfield for the imidazolium ring in the methylethylimidazolium chloride melt are gradually replaced with but a single proton resonance, since only the proton on ring position 2 remains after reaction.

Figure 10 shows the change in the decoupled ^{13}C NMR spectrum with time as the reaction proceeds at room temperature. These spectra show that the reaction proceeds cleanly to give a quantitative yield of product. At the intermediate time of 70 minutes, the three upfield ^{13}C resonances for the NCH_3 and NCH_2CH_3 carbons (refer to Figure 1) now show four resonances each. These resonances are consistent with the predicted reactions and correspond to the starting material, the two monochloro-substituted

intermediates, and the dichloro-substituted product. The final spectrum at 7 hours shows the reaction is complete with no apparent reactant or side products present.

5. Redistribution of Halide upon Mixing of Acidic Chloride and Bromide Melts in Acetonitrile Solvent

Acidic $AlBr_3$/1-methyl-3-ethylimidazolium bromide melts were prepared from 1-methyl-3-ethylimidazolium bromide and aluminum bromide. Several drops of a bromide melt, 0.60 mole fraction in $AlBr_3$, were added to several drops of a corresponding $AlCl_3$/1-methyl-3-ethylimidazolium chloride melt in dry acetonitrile, and the ^{27}Al NMR spectrum taken at room temperature. This spectrum (Figure 11) shows evidence of a quantitative redistribution of halide on aluminum. There are five resonances downfield from the external $Al(H_2O)_6^{+3}$ reference in a chemical shift region known to be specific for tetracoordinated aluminum halide anions in acetonitrile solvent.[13] The resonance furthest downfield at 102.57 ppm corresponds to the chemical shift of $AlCl_4^-$ when only the chloride melt is present in acetonitrile, while the resonance at 79.67 ppm corresponds to the chemical shift of $AlBr_4^-$ when only the bromide melt is present in acetonitrile. The intermediate ^{27}Al resonances undoubtedly correspond to $AlCl_3Br^-$ at 98.86 ppm; $AlCl_2Br_2^-$ at 93.84 ppm; and $AlClBr_3^-$ at 87.46 ppm. Interestingly, when the same acidic bromide melt is in contact with carbon tetrachloride in acetonitrile solution, the same pattern of five ^{27}Al resonance are observed, showing the exchange of bromine and chlorine between carbon tetrachloride and the melt.

ACKNOWLEDGEMENT

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Table 1.

^{27}Al Chemical Shifts (δ) at 90° for Various Compositions

Mole Fraction $AlCl_3$	δ ppm
0.0	149.46
0.109	149.10
0.201	149.03
0.270	148.77
0.340	148.33
0.420	147.97
0.480	147.25
0.500	146.74
0.527	146.56
0.560	146.415
0.617	146.18
0.659	145.98

Table 2.

^{27}Al Linewidths ($\Delta\nu_{1/2}$) at 90° for Various Compositions

Mole Fraction $AlCl_3$	$\Delta\nu_{1/2}$ Hz
0.11	231
0.20	202
0.27	176
0.34	110
0.42	39.8
0.48	30.5
0.50	2.34
0.53	87.5
0.56	277
0.62	504
0.66	655

Table 3.

^{27}Al Linewidths ($\Delta\nu_{1/2}$) and Viscosities (η) at 30° for Various Compositions

Mole Fraction $AlCl_3$	$\Delta\nu_{1/2}$ Hz	η
0.5073	140.38	15.37
0.5195	383.91	15.08
0.5283	534.62	14.87
0.5379	747.07	14.65
0.5514	913.80	14.33
0.5716	1091.3	13.86
0.5870	1286.7	13.50
0.6009	1501.4	13.18
0.6154	1696.8	12.43
0.6302	1782.2	10.99
0.6415	1965.3	9.88
0.6525	2172.9	8.80

Fig. 1 NMR SPECTRA OF NEAT MELT & MELT IN PHOSPHORYL CHLORIDE SOLUTION

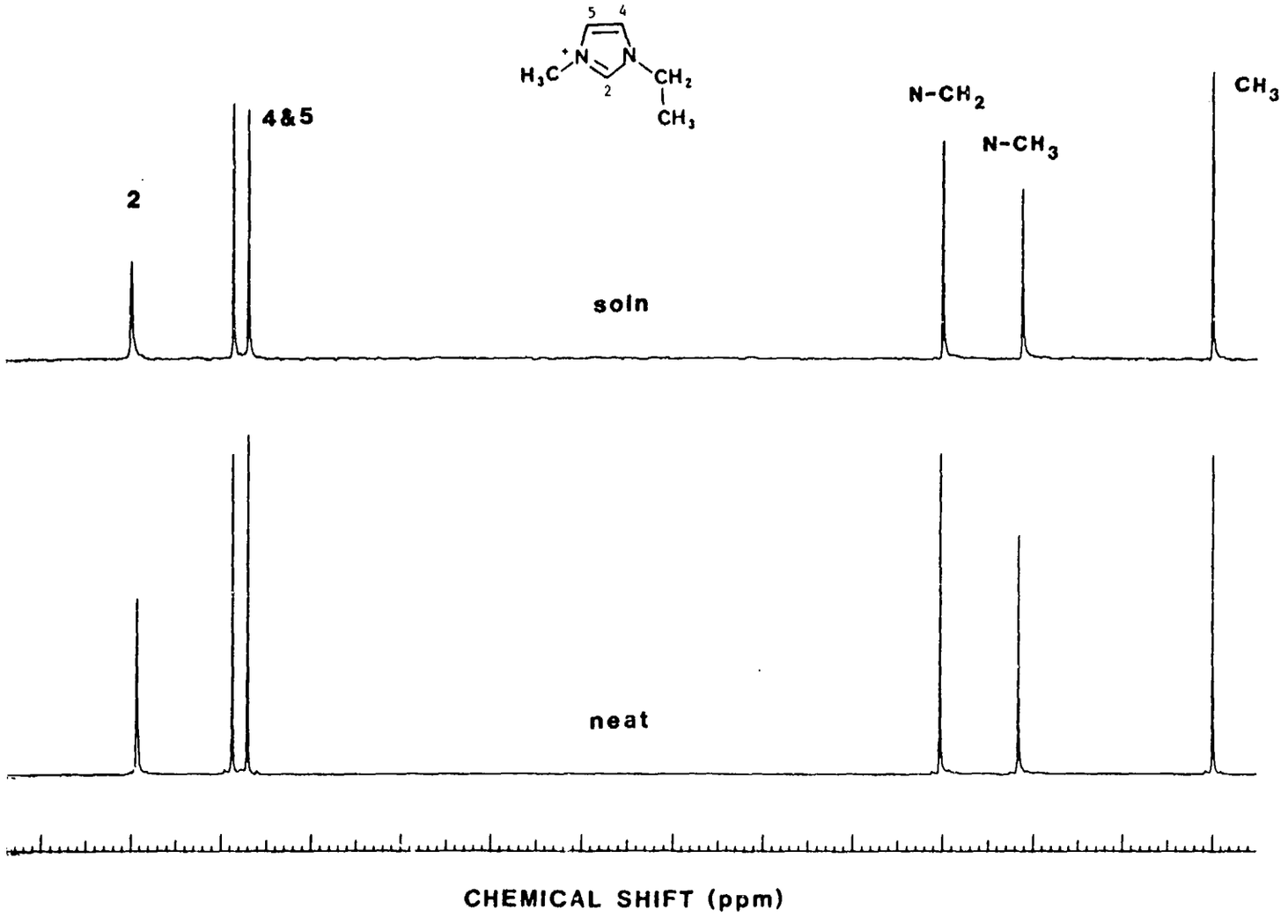
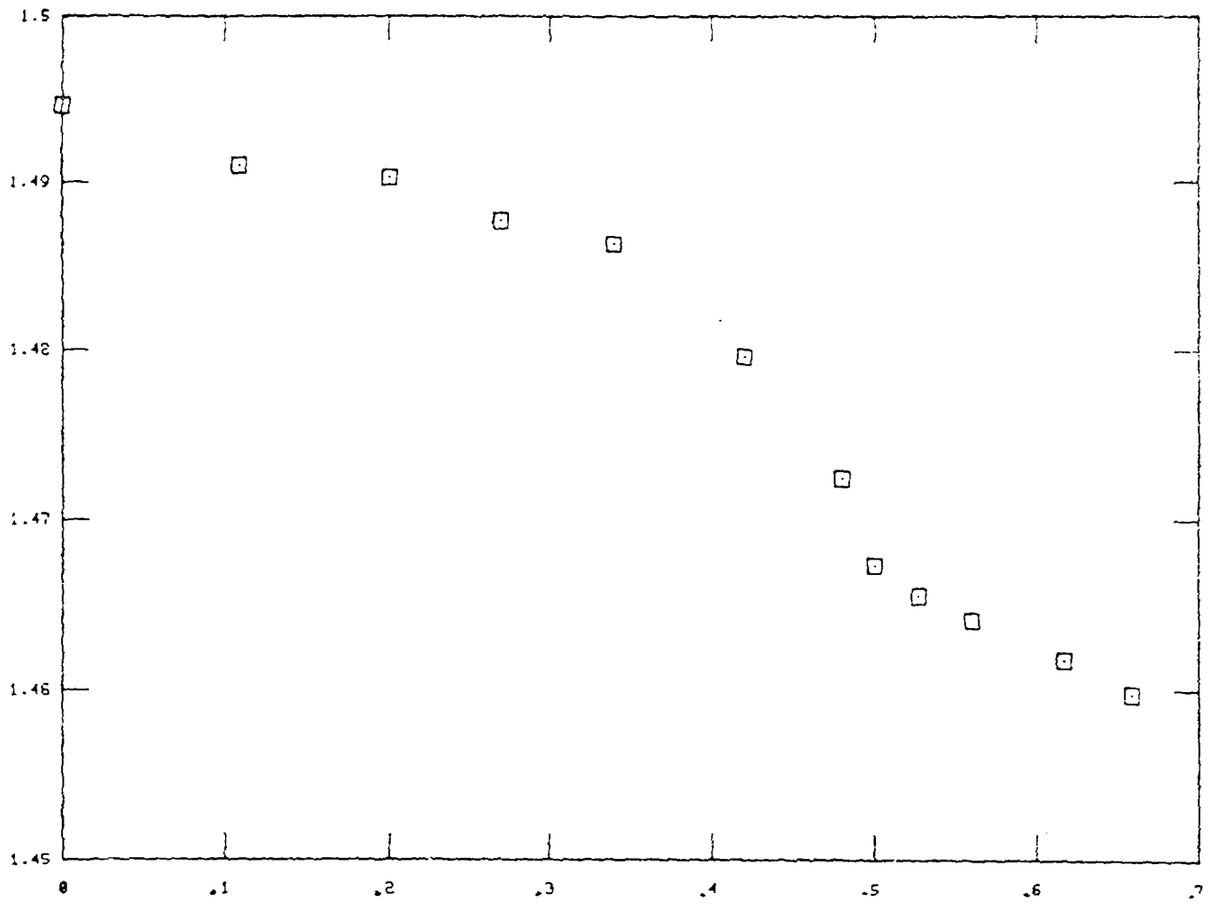


FIG. 2 C-13 CHEMICAL SHIFTS OF CARBON-2 IN CHLORIDE MELTS



CHEM SHIFT
(ppm/100)

MOLE FRACTION OF ALUMINUM CHLORIDE

FIG. 3 C-13 SHIFTS OF CARBON-2 IN BASIC CHLORIDE MELTS

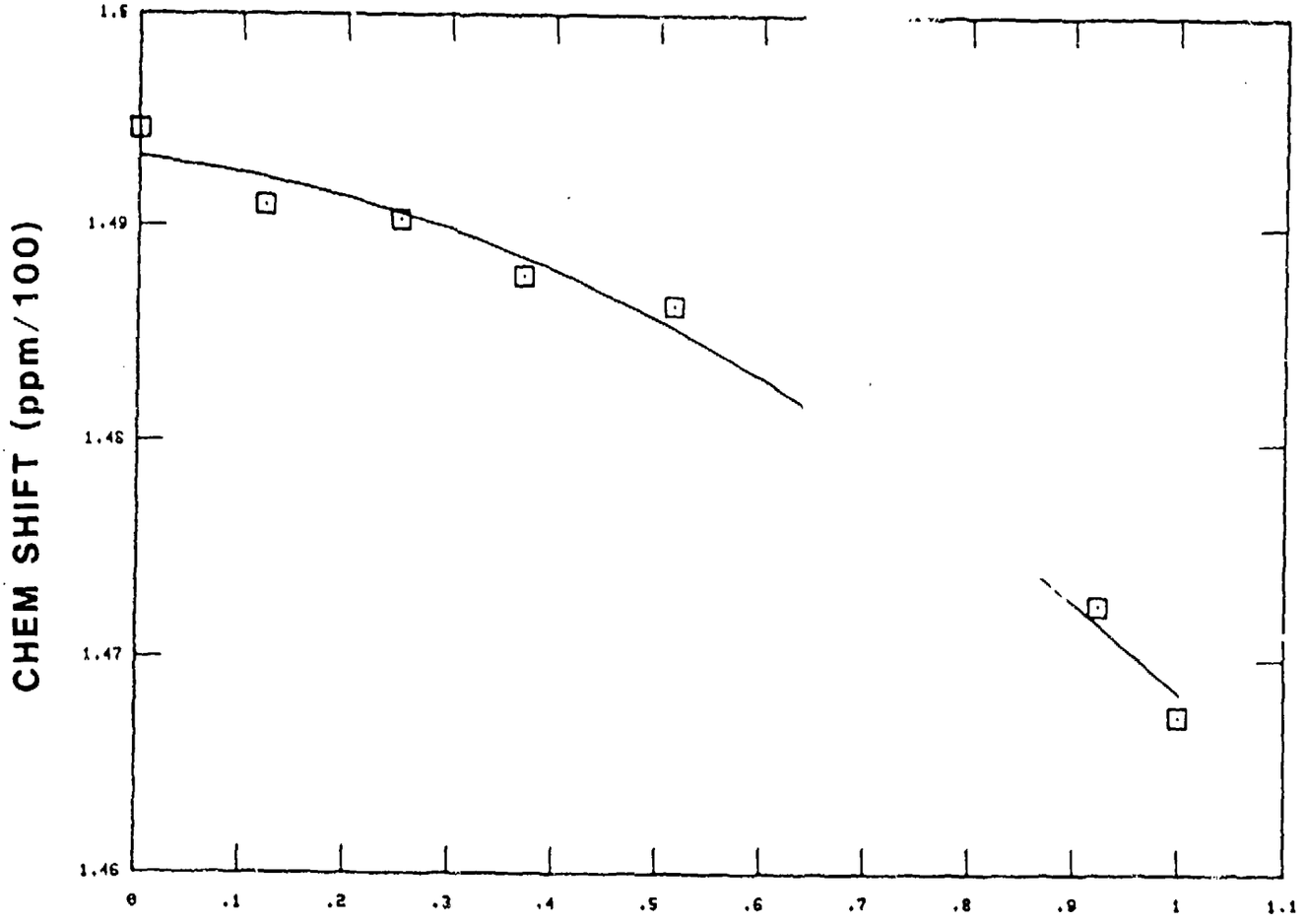


Fig. 4 Al-27 NMR SPECTRA OF CHLORIDE MELT (m.f. $AlCl_3$ 0.56) AT VARIOUS PREACQUISITION DELAY TIMES

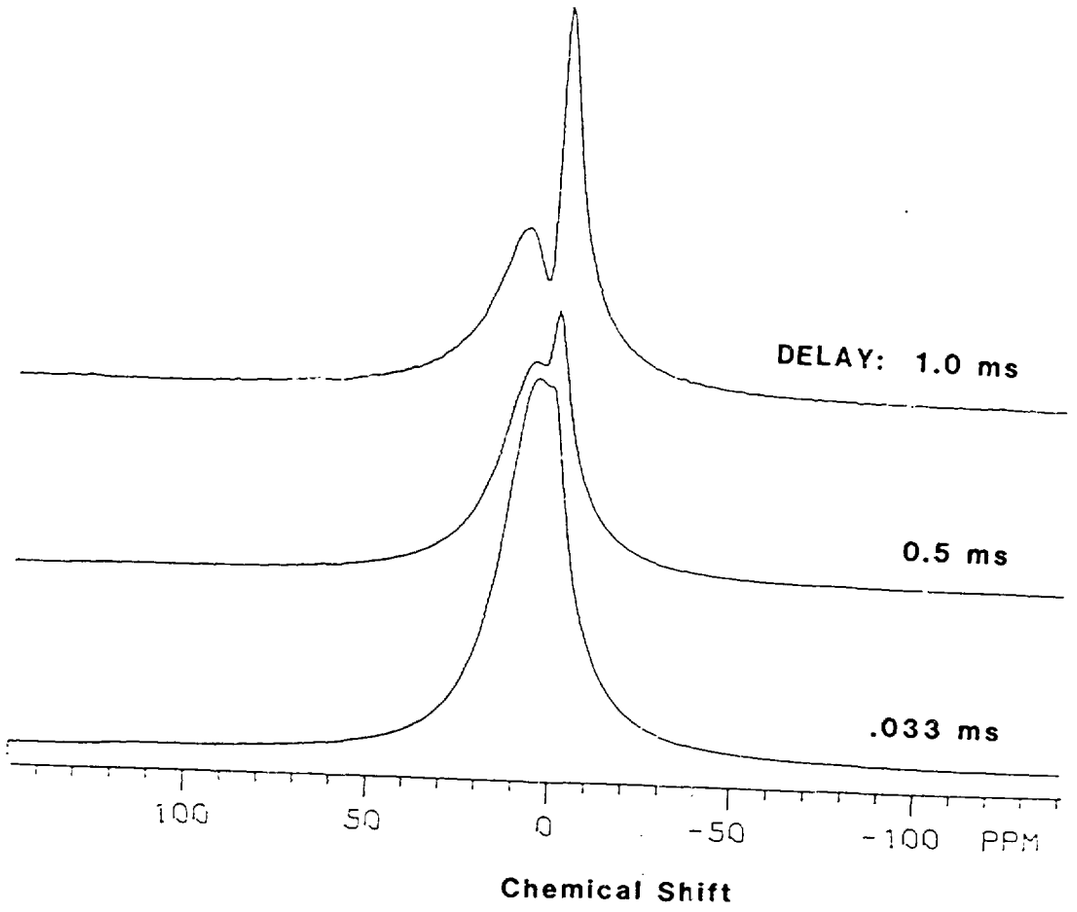
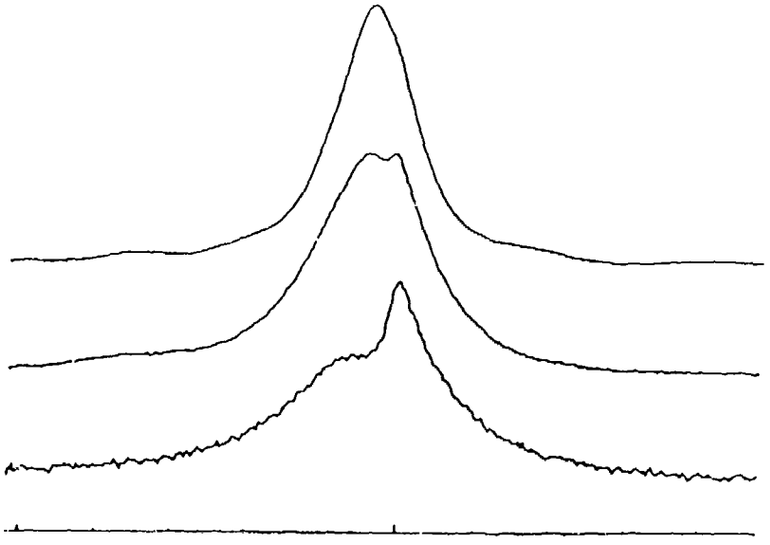


Fig. 5 TEMP. DEPENDENCE OF Al-27 NMR SPECTRA (m.f. $AlCl_3$ 0.60)



(Temp. bottom to top: 47, 67 and 88°)

Fig. 6 CALCULATED Al-27 NMR SPECTRA (scale same as Fig. 5)

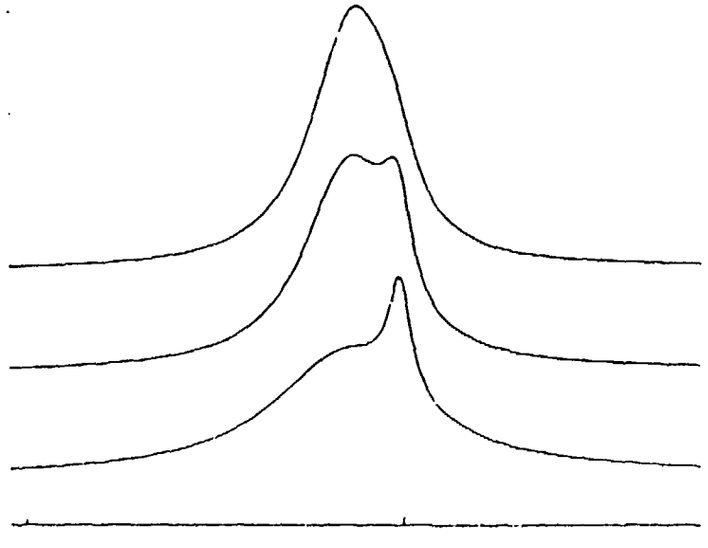


Fig. 7 Al-27 LINEWIDTHS VS MOLE FRACT. TETRACHLOROALUMINATE

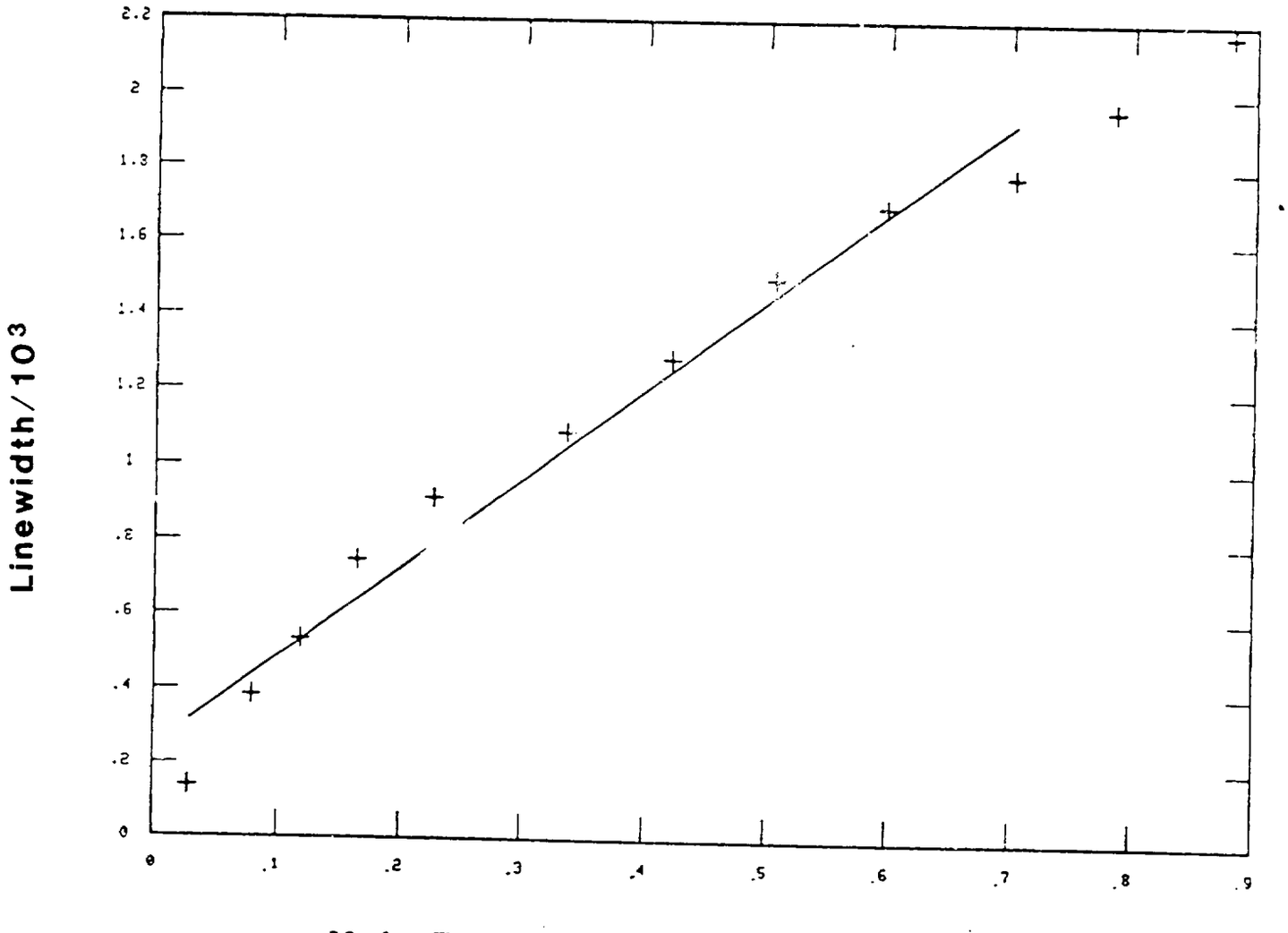


Fig. 8 Al-27 LINEWIDTH/ABS. VISC. VS MOLE FRACT. TETRACHLOROALUMINATE

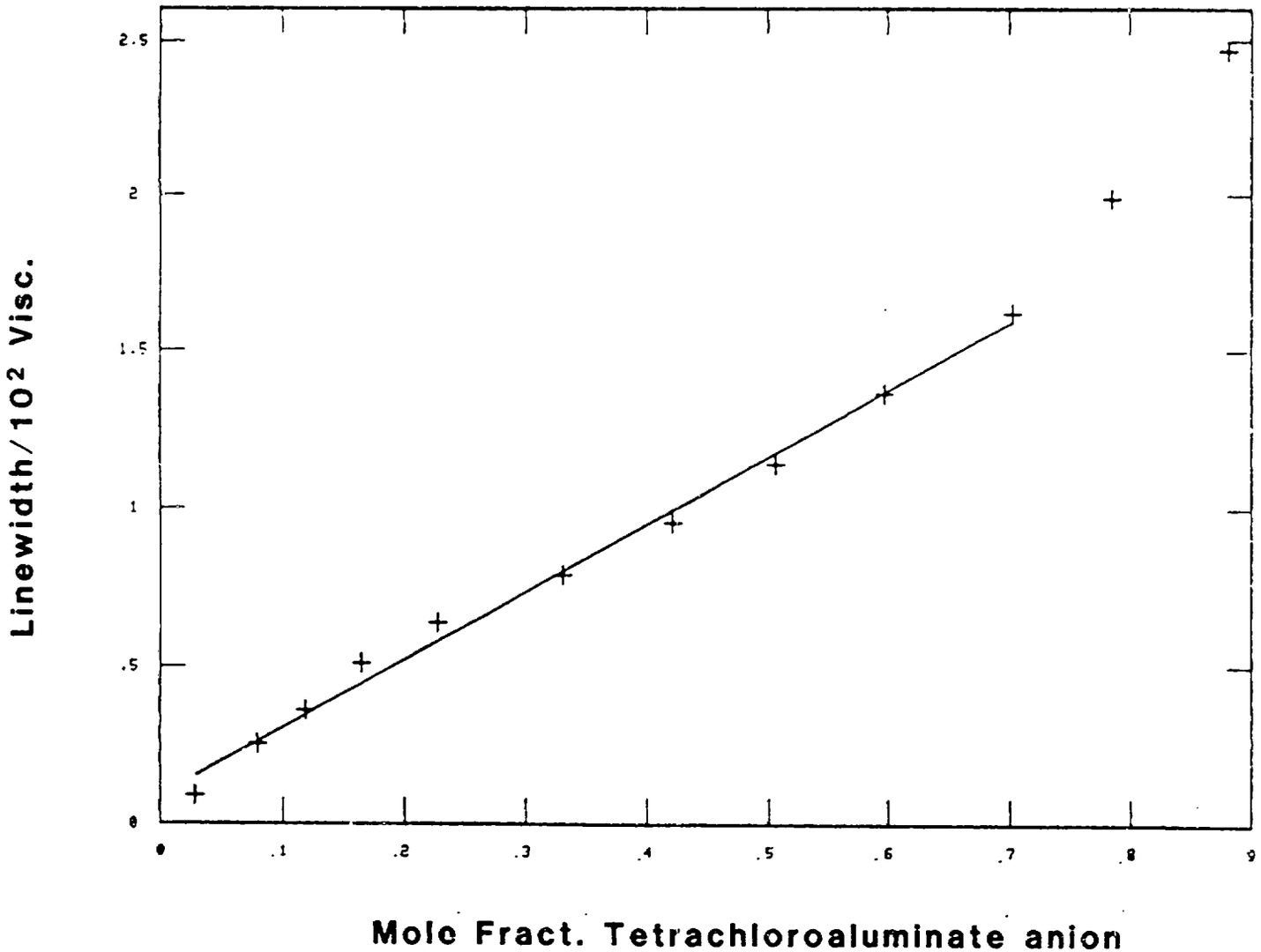


Fig. 9 PROTON NMR SPECTRA OF CHLORIDE MELT (m.f. $AlCl_3$ 0.60) + Cl_2

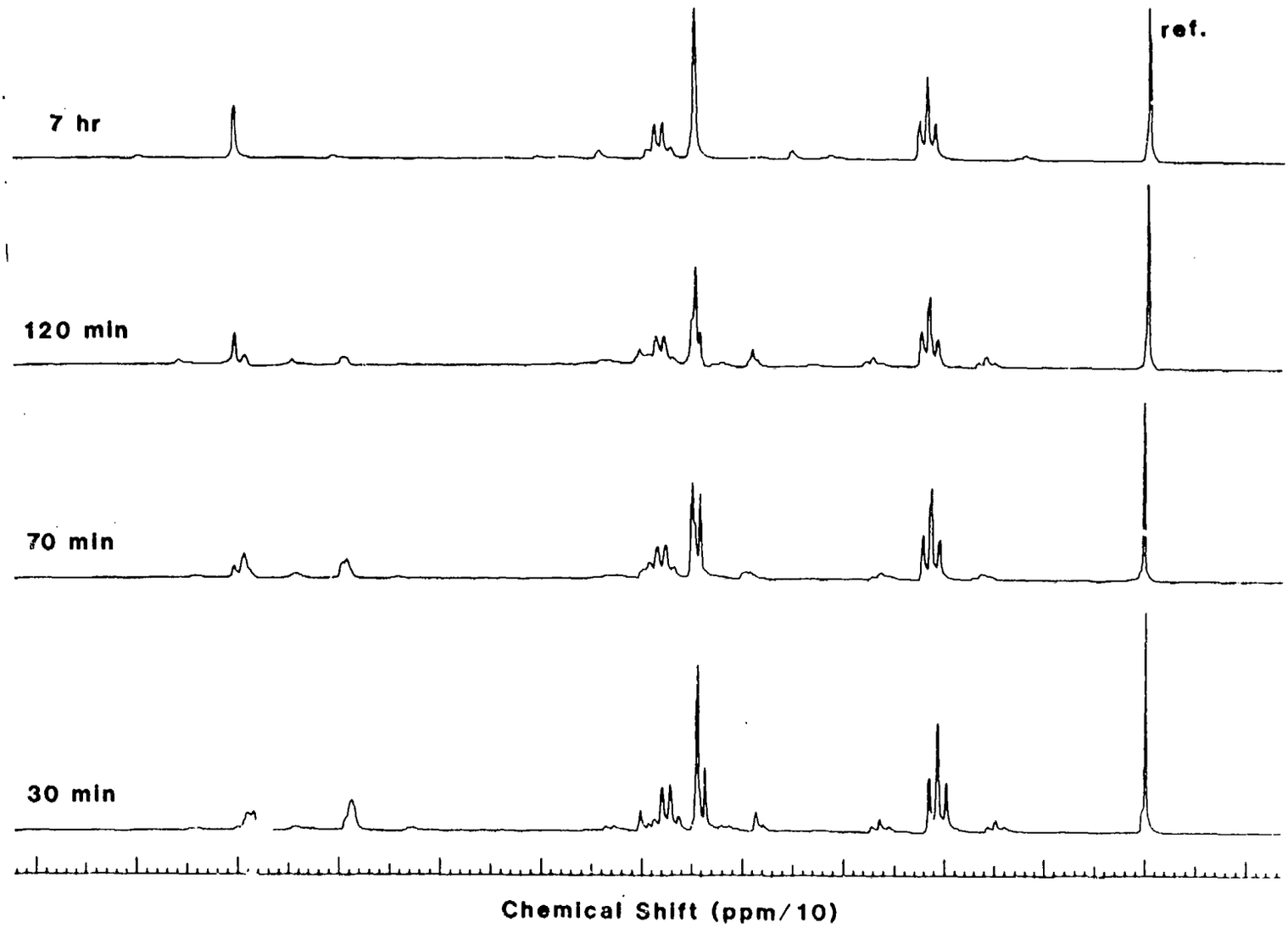


Fig. 10 C-13 NMR SPECTRA OF CHLORIDE MELT (m.f. $AlCl_3$ 0.60) + Cl_2

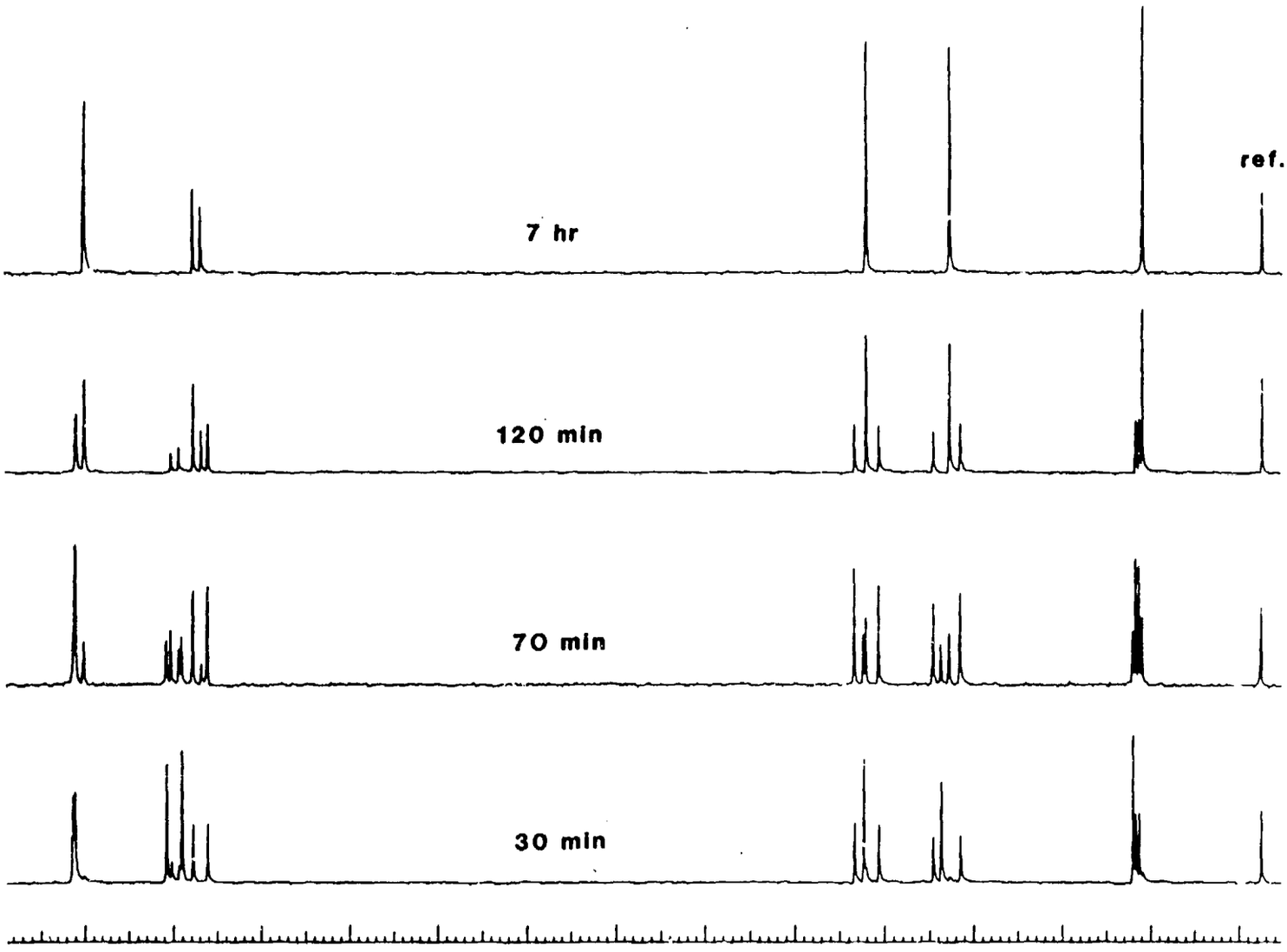
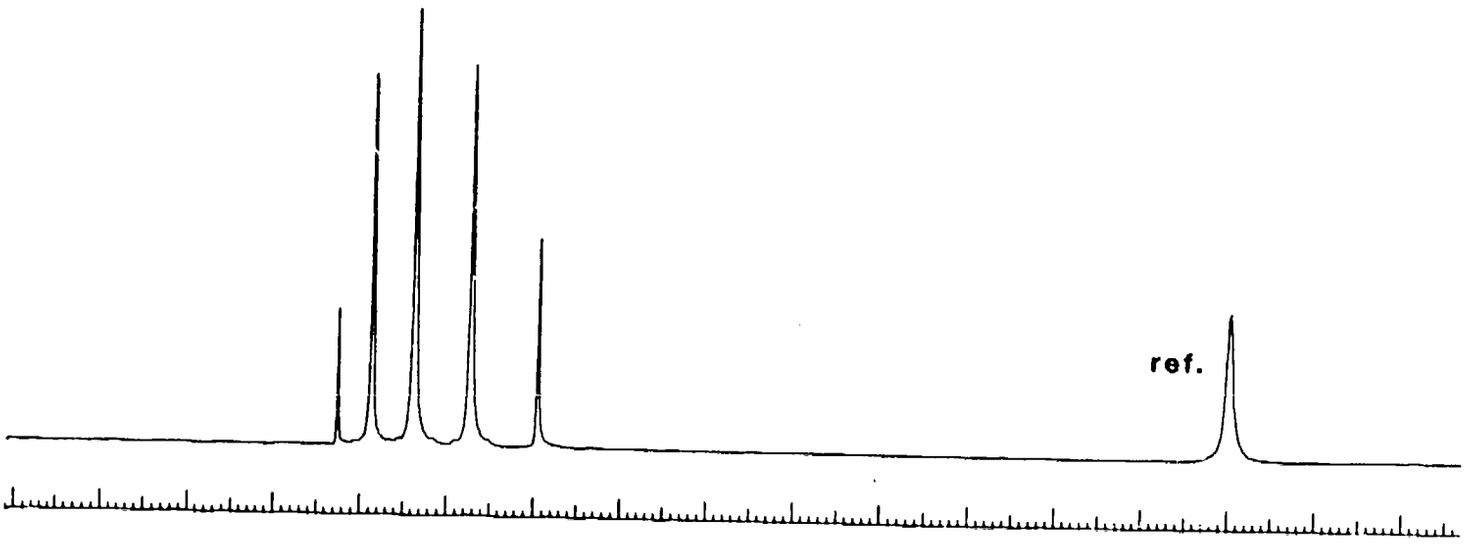


Fig. 11 CHLORIDE MELT & BROMIDE MELT IN ACETONITRILE



```
MUSE          13-JAN-1984 10:36

1000 REM N SITE EXCHANGE MATRIX METHOD 12/20/83
1010 DIM P$(40),U(40)
1020 DEF FN.SEEK%(Z$)
1030 M%=0% \ FOR X%=1% TO PX% \IF POS(P$(X%),Z$,1)=1 THEN M%=X% \ X%=PX%
1040 NEXT X% \FN.SEEK%=M%\ FNEND
1050 DEF FN.PAR(Q$)
1060 Z%=FN.SEEK%(Q$) \ IF Z%>0% THEN 1090
1070 PX%=PX%+1% \ P$(PX%)=Q$ \ Z%=PX% \PRINT Q$;\INPUT U(Z%)
1080 CHG%=PX%
1090 FN.PAR=U(Z%) \ FNEND
1100 ON ERROR GOTO 1870
1110 IE%=2% \ Y$=TRM$(Y$)
1120 IF Y$="" THEN LINPUT "PARAMETER FILE";Y$
1130 IF POS(Y$,".",1)<1 THEN Y$=Y$+".PAR"
1140 OPEN Y$ FOR INPUT AS FILE#2
1150 INPUT#2,P$(0),U(0) \ IF P$(0)<>"SITES" THEN 1910
1160 PRINT "MUSE PARAMETERS:" \ PRINT \ PRINT P$(0);" = ";U(0)
1170 NS%=U(0)
1180 IF NS%>9% THEN PRINT "*** TOO MANY SITES (9 MAX) ***" \ GOTO 1920
1190 DECLARE DOUBLE QN(9,9),QM(9,9),QR(9,9)
1200 DECLARE DOUBLE QQ(9,9),QX(9,9),P(9,9),QZ(1,1)
1210 DECLARE DOUBLE QY(9,1),QL(1,9),K(9,9)
1220 DECLARE DOUBLE QD(9,9),NU(1,9),QB(9,9)
1230 MAT QM=ZER(NS%,NS%) \ MAT QN=ZER(NS%,NS%) \ MAT QB=ZER(NS%,NS%)
1240 MAT K=ZER(NS%,NS%) \ MAT P=ZER(1,NS%) \ MAT T=ZER(1,NS%)
1250 MAT F=ZER(1,NS%) \ MAT NU=ZER(1,NS%)
1260 XP%=NS%*4%+3%
1270 IE%=3% \ PX%=0%
1280 FOR I%=1% TO XP% \ INPUT#2,P$(I%),U(I%) \PX%=PX%+1%
1290 PRINT P$(I%);" = ";U(I%) \ NEXT I%
1300 CLOSE #2 \ PRINT

Ready
```

```
MUSE          13-JAN-1984 10:37

1310 IE%=1%
1320 WIDTH=FN.PAR('WID') \ SYM%=FN.PAR('SYM') \ OFFSET=FN.PAR('OFF')
1330 FOR I%=1% TO NS%
1340 SS$=SEG$(STR$(I%),1,1)
1350 F(1,I%)=FN.PAR('F'+SS$)
1360 P(1,I%)=FN.PAR('P'+SS$)
1370 T(1,I%)=FN.PAR('T'+SS$)
1380 NEXT I%
1390 FOR I%=1% TO NS%
1400 SS$=SEG$(STR$(I%),1,1)
1410 FOR J%=I%+1% TO NS%
1420 KP=FN.PAR('K'+SS$+SEG$(STR$(J%),1,1))
1430 K(I%,J%)=KP*P(1,J%) \ K(J%,I%)=KP*P(1,I%)
1440 NEXT J% \ NEXT I%
1450 INPUT 'PARAMETER TO CHANGE';X$ \ IF X$='' THEN 1500
1460 I%=FN.SEEK%(X$) \IF I%>0% THEN 1480
1470 PRINT 'NO PARAMETER >>>> ';X$ \ GOTO 1450
1480 PRINT 'NEW VALUE FOR ';P$(I%); \ INPUT V(I%)
1490 CHG%=I% \ GOTO 1320
1500 XX=0\FOR I%=1% TO NS%\XX=P(1,I%)+XX\NEXT I%
1510 IF (XX<1) AND P(1,NS%)=0 THEN P(1,NS%)=1-XX \ XX=1.0
1520 IF XX=1 THEN 1550
1530 P(1,I%)=P(1,I%)/XX FOR I%=1% TO NS%
1540 PRINT 'POPULATIONS NORMALIZED',P(1,1%),P(1,2%),P(1,3%)
1550 PRINT \ IF CHG%=0% THEN 1590
1560 OPEN Y$ FOR OUTPUT AS FILE #2
1570 PRINT#2,P$(I%);',';STR$(V(I%)) FOR I%=0% TO PX%
1580 CLOSE #2 \ PRINT 'PARAMETERS SAVED AS NEW VERSION OF ';Y$
1590 PRINT \ PRINT 'BEGINNING SPECTRUM CALCULATIONS'\PRINT
1600 X=-WIDTH*3.1415927 \N9%=500%\DX=ABS(2*X/N9%) \N%=2%

Ready
```

```
1610 IF (SYM%<13) AND (SYM%>8) THEN A$=STR$(INT(SYM%))+':' ELSE A$='9:'
1620 MAT QY=CON(NS%,1)
1630 X$(1)='NU'\U$(1)='HZ'\M(1)=0 \ X$(2)='INTEN'\U$(2)='ARB' \ M(2)=0
1640 C$=STR$(NS%)+'-SITE EXCHANGE'
1650 MAT QM=K
1660 FOR I%=1% TO NS% \ QM=0
1670 FOR J%=1% TO NS%
1680 QM=QM-K(I%,J%) IF I%<>J%
1690 NEXT J%
1700 QM(I%,I%)=-1/T(1,I%)+QM
1710 NEXT I%
1720 MAT QR=INV(QM)
1730 MAT NU=(6.2831853)*F
1740 FOR IT%=0% TO N9%-1%\KK%=IT%*N%-1%
1750 X(KK%+1%)=X*.1591549\MAT QN=ZER
1760 FOR I%=1% TO NS%
1770 QN(1%,I%)=X-NU(1,I%)
1780 NEXT I%
1790 MAT QQ=QR*QN \ MAT QB=QN*QQ
1800 MAT QD=QM+QB \ MAT QX=INV(QD)
1810 MAT QL=QX*QY \ MAT QZ=P*QL
1820 X(KK%+2%)=-QZ(1,1)+OFFSET
1830 X=X+DX
1840 A$(IT%)=A$
1850 NEXT IT%
1860 A$(0)='8:' \ GOTO 1930
1870 IF (ERR=11) AND IE%=3% THEN RESUME 1300
1880 PRINT 'ERROR ';ERR;' IN LINE ';ERL;'  ';ERT$(ERR)
1890 RESUME 1900
1900 ON IE% GOTO 1920,1910

Ready
```

```
MU E          13-JAN-1984 10:38

1910 PRINT 'BAD PARM FILE' \Y$+"'\ GOTO 1120
1920 PRINT 'ABNORMAL EXIT'
1930 REM END OF USER PROGRAM

Ready
```